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(54) Title: THERMAL TRANSFER IMAGE RECEIVING SHEET AND METHOD

(57) Abstract: A thermal transfer image-receiving polymeric sheet capable of recording thereon thermally transferred dye or ink images in a clear and sharp form. The image-receiving layer comprises at least one water dispersible aliphatic polyether-polyurethane resin and a silica dispersion.

TITLE: THERMAL TRANSFER IMAGE RECEIVING SHEET AND METHOD

FIELD OF THE INVENTION

The present invention relates to a thermal transfer image-receiving sheet. More particularly, the present invention relates to a matte finish thermal transfer image-receiving polymeric sheet capable of recording thereon thermally transferred dye or ink images in a clear and sharp form.

BACKGROUND

In thermal transfer recording systems an ink ribbon is heated through a thermal head or by laser or the like in accordance with image information. The heating causes thermal melting, thermal diffusion or sublimation, by which a dye is transferred from the ink ribbon onto a printing sheet to form an image on the printing sheet.

The printing sheet generally is made up of a support film having a dye receiving layer coated thereon. The dye receiving layer is a layer that receives a dye or ink transferred thereto from the ink ribbon by heating and preserves an image formed from the dye. Typical dye receiving layers for polymeric substrates comprise at least one dye receptive resin dissolved in an organic solvent. Examples of such solvent borne resins include polyester, polycarbonate, polyvinyl chloride, vinyl chloride copolymers such as vinyl chloride-vinyl acetate copolymer, and thermoplastic resins such as polyurethane resin, polystyrene, acrylic-styrene (AS) resin, acrylonitrile-butadiene-styrene (ABS) resin, and the like.

It may be desirable to reduce or eliminate the use of volatile organic solvents in the process for manufacturing polymeric image receiving sheets. In particular, it may be desirable to employ an aqueous composition for producing an image receiving layer on a polyester substrate without compromising image clarity and durability.

SUMMARY

According to one aspect of the invention, a printing sheet of the type that is used in a thermal transfer recording system is provided. The printing sheet comprises a polymeric film support, and a matte finish image receiving layer formed on the film support. The image receiving layer may be formed from a coating of an aqueous coating composition. In one embodiment, the aqueous coating composition comprises an aqueous dispersion of an aliphatic polyether-polyurethane and a silica dispersion. An aqueous crosslinking agent may be added to the aqueous coating composition.

According to another aspect of the invention, a dye receiving coating composition is provided. In one embodiment, the dye receiving coating composition comprises an aqueous dispersion of an aliphatic polyether-polyurethane resin and a silica dispersion.

According to yet another aspect of the invention, a method of preparing a matte finish thermal transfer image receiving sheet is provided. The method provides for coating a substrate sheet surface with the aqueous coating composition.

BRIEF DESCRIPTION OF THE DRAWINGS

In the accompanying drawings:

Fig. 1 is a schematic view illustrating a cross-section of a thermal transfer image receiving sheet according to the present invention.

DETAILED DESCRIPTION

A first embodiment of the thermal transfer image receiving sheet of present invention may be described in reference to Fig. 1. Fig. 1 is a schematic view of a cross section of one example of a thermal transfer image receiving sheet 1 that includes substrate sheet 2 and a dye receiving layer 3 disposed on one surface of the substrate sheet 2.

The substrate sheet 2 may be formed from sheet materials selected with reference to application specific criteria. Such criteria may include, for example, desired dimensions (height, length and thickness), surface texture, composition, flexibility, and other physical and economic attributes or properties. Suitable sheet

materials may include, for example, synthetic papers such as polyolefin type, polystyrene type; wood free paper; art paper; coat paper; cast coat paper; wall paper; lining paper; cellulose fiber paper such as paperboard; various plastic films or sheets such as polyolefin, polyvinyl chloride, polyethylene terephthalate, polystyrene, polymethacrylate and polycarbonate.

In one embodiment, the substrate sheet 2 may be, or may include, a multilayer polymeric sheet. The multi-layers may be coextruded, or the multi-layers may be laminated together. In one embodiment, the substrate sheet 2 includes both co-extruded multi-layers and laminated multi-layers.

In addition, a white opaque film may be formed by adding a white pigment to one or more of the aforementioned synthetic resins and used as the substrate sheet 2. In one embodiment, a foamed film is used as the substrate sheet 2. The foamed film may be formed by a conventional foaming operation. In one embodiment, the substrate sheet 2 may be a laminated body formed by combining a plurality of single-layered sheets composed of the above listed materials. Examples of such a laminated body may include the combination of cellulose fiber paper with synthetic paper, and a laminated body of combined cellulose fiber paper with a plastic film or sheet.

The thickness of the substrate sheet 2, formed in the manner as mentioned above, may be determined with reference to application specific criteria. Such criteria may include the desired end use. In one embodiment, the sheet thickness is in a range of from about 10 microns or micrometers (μm) to about 300 μm. In one embodiment, the sheet thickness is in a range of from about 20 micrometers or microns (μm) to about 200 μm. In one embodiment, the sheet thickness is in a range of from about 30 micrometers or microns (μm) to about 150 μm.

A primer treatment or a corona discharging treatment may be used on the substrate sheet 2 to increase a bonding strength between the substrate sheet 2 and the dye receptor layer 3 to be formed on a surface of the substrate sheet 2.

An intermediate layer (not shown) may be provided between the dye receptor layer 3 and the substrate sheet 2 to impart preselected properties. Such properties may include an adhesion property, whiteness or brightness, cushioning property, antistatic property, shielding property, anti-curling property, and the like.

A back surface layer (not shown) may be provided onto a surface opposite the surface of the substrate sheet 2 to which the dye receiving layer 3 is formed. The back surface layer may impart preselected properties to the thermal transfer image receiving sheet 1. The properties may include, for example, an enhanced conveying fitness, an enhanced writing property, pollution resistance, anti-curling property, and the like. If desired, an antistatic layer (not shown) containing a commercially available antistatic agent may be provided on the dye receiving layer 2 or the back surface layer to improve the antistatic property of the thermal transfer image receiving sheet 1.

The dye receiving layer 2 comprises a coating formed from an aqueous composition. In one embodiment, the aqueous coating composition includes at least one water dispersible aliphatic polyether-polyurethane resin and a silica dispersion. The dispersion may comprise colloidally dispersed particles of the polyurethane polymers.

In one embodiment, the polyether-polyurethane polymer is the reaction product of a predominantly aliphatic polyisocyanate component and a polyether polyol component. As used herein, the term "predominantly aliphatic" means that at least 70 weight percent of the polyisocyanate component is an aliphatic polyisocyanate, in which all of the isocyanate groups are directly bonded to aliphatic or cycloaliphatic groups, irrespective of whether aromatic groups are also present. More preferably, the amount of aliphatic polyisocyanate is at least 85 weight %, and most preferably, 100 weight %, of the polyisocyanate component. Examples of suitable aliphatic polyisocyanates include ethylene diisocyanate, 1,6-hexamethylene diisocyanate, isophorone diisocyanate, cyclohexane-1,4-diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, cyclopentylene diisocyanate, p-tetra-methylxylene diisocyanate (p-TMXDI) and its meta isomer (m-TMXDI), hydrogenated 2,4-toluene diisocyanate, and 1-isocyanto-1-methyl-3(4)-isocyanatomethyl cyclohexane (IMCI). Mixtures of aliphatic polyisocyanates can be used. Suitable polyether polyols include products obtained by the polymerization of a cyclic oxide or by the addition of one or more such oxides to polyfunctional initiators. Such polymerized cyclic oxides include, for example, ethylene oxide, propylene oxide and tetrahydrofuran. Such polyfunctional initiators having oxides added include, for

example, water, ethylene glycol, propylene glycol, diethylene glycol, cyclohexane dimethanol, glycerol, trimethylopropane, pentaerythritol and Bisphenols (such as A and F).

Commercially available polyether-polyurethanes useful in the present invention include those sold under the trade names SANCURE 878, AVALURE UR-450 and SANCURE 861 by Goodrich Corporation (Charlotte, NC), and NEOREZ R-551 and NEOREZ R-563 by NeoResins (Waalwijk, The Netherlands).

The dye receiving layer 3 may include a water dispersible crosslinker. Suitable water-dispersible polyfunctional chemically activatable crosslinking agents are commercially available. These crosslinking agents include dispersible formulations of polyfunctional aziridines, isocyanates, melamine resins, epoxies, oxazolines, carbodiimides and other polyfunctional crosslinkers. In one embodiment, the crosslinking agents are added at an amount in a range of from about 0.1 parts to about 10 parts based on 100 parts total solids. In one embodiment, the crosslinking agents are added at an amount in a range of from about 0.2 parts to about 5 parts based on 100 parts total solids. Adding crosslinking agents to the polyurethane dispersion composition may form an interpenetrating or interconnected network having crosslinked matrixes is formed which link the blended polymers with covalent and/or non-covalent linkages.

A matting agent useful in the composition comprises silica dispersion. In one embodiment, silica particles in an amount of from about 2.0% to about 15% (solids) by weight are added to the composition. In one embodiment, silica particles in an amount of from about 4% to about 8% (solids) by weight are added to the composition. The silica is typically added as an aqueous dispersion. Useful commercially available silica matting agents include the SYLOID® C-Series silica gel matting agents from W.R. Grace.

Pigments may be added to the composition to increase the opacity and/or modify the porosity of the coated substrate. In one embodiment, white pigment is added to the coating composition. Other additives such as waxes, defoamers, antioxidants, UV stabilizers, etc. may be included in the composition to obtain a certain desired characteristic.

A thermal transfer image-receptive coated product can be made by applying a thermal transfer image-receptive composition as described above to one or both surfaces of a face stock or label stock using conventional coating or other application technique. Non-limiting examples of such techniques include slot die, air knife, brush, curtain, blade, floating knife, gravure, kiss roll, knife-over-blanket, knife-over-roll, off set gravure, reverse roll, reverse-smoothing roll, rod, and squeeze roll coating.

In general, dry coat weight of the coated composition is greater than about 1.0 g/m^2. In one embodiment, the dry coat weight of the image receiving layer is in the range of from about 1.1 g/m^2 to about 10 g/m^2, or about 2 g/m^2 to about 5 g/m^2.

EXAMPLE

The following example is intended only to illustrate methods and embodiments in accordance with the invention, and as such should not be construed as imposing limitations upon the claims.

Example 1

A coating composition comprising the ingredients listed in Table 1 is prepared as follows:

Ingredient	**Wt. %**
Polyurethane dispersion NEOREZ R-563: aliphatic polyether urethane dispersion, 35,.5% solids)	18.6
Silica SYLOID C 503 (100% solids)	6.5
White pigment	9.3
Water	65.3
Crosslinker CX-100: polyfunctional aziridine crosslinker	0.2

The coating composition is coated onto a 2 mil polyethylene terephthalate (PET) substrate web. The coating is dried at a temperature of about 90°C and a line speed of about 120 meters/minute to form an image receiving layer. The dry coat weight of the image receiving layer is about 2.5 g/m^2.

The coating composition of Example 1 is also coated onto a matte chrome, biaxially oriented PET substrate having a thickness of about 2 mils, and onto a white, biaxially oriented PET substrate having a thickness of about 2 mils.

While the invention has been explained in relation to embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims, and to cover insubstantial variations thereof.

What is claimed is:

1. A thermal transfer image receiving sheet comprising:

a substrate sheet; and

an image receiving resinous layer on at least one surface of the substrate sheet, the image receiving resinous layer having a dry coat weight greater than about 1 g/m^2 and comprising a dye receiving resinous material;

wherein the dye receiving resinous material comprises (a) at least one water dispersible aliphatic polyether-polyurethane and (b) water dispersible silica particles in an amount of about 2% to about 15% by weight.

2. The thermal transfer image receiving sheet of claim 1 wherein the substrate sheet comprises polyester.

3. The thermal transfer image receiving sheet of claim 2 wherein the substrate sheet comprises polyethylene terephthalate.

4. The thermal transfer image receiving sheet of any one of the preceding claims wherein polyether-polyurethane resin (a) comprises the reaction product of an aliphatic polyisocyanate component and a polyether polyol component.

5. The thermal transfer image receiving sheet of any one of the preceding claims wherein the image receiving resinous layer has a dry coat weight of about 1.1 g/m^2 to about 10 g/m^2.

6. The thermal transfer image receiving sheet of any one of the preceding claims wherein the image receiving resinous layer has a matte finish.

7. A dye receiving coating composition comprising:

(a) at least one aqueous dispersion of an aliphatic polyether-polyurethane resin; and

(b) water dispersible silica particles in an amount of about 2% to about 15% by weight.

8. The dye receiving coating composition of claim 7 further comprising a multifunctional crosslinking agent.

9. The dye receiving coating composition of claim 8 where the multifunctional crosslinking agent comprises a polyfunctional aziridine.

10. The dye receiving coating composition of any one of claims 7 to 9 wherein the coating composition is substantially organic solvent free.

11. The dye receiving coating composition of any one of claims 7 to 9 wherein dispersion (a) comprises the reaction product of an aliphatic polyisocyanate component and a polyether polyol component.

12. A method of forming a thermal transfer image receiving sheet having a matte finish comprising:

coating a substrate sheet surface with an aqueous coating composition, the aqueous coating composition comprising at least one water dispersible aliphatic polyether-polyurethane resin, a water dispersible silica, and an aqueous crosslinking agent;

drying the aqueous coating composition to form a thermal transfer image receiving sheet having a dry coat weight of greater than about 1 g/m and having a matte finish.

13. The method of claim 12 wherein the substrate sheet comprises polyester.

14. The method of claim 13 wherein the substrate sheet comprises polyethylene terephthalate.

15. The method of any one of claims 12 to 14 wherein polyether-polyurethane resin (a) comprises the reaction product of an aliphatic polyisocyanate component and a polyether polyol component.

16. The method of any one of claims 12 to 15 wherein the image receiving resinous layer has a dry coat weight of about 1.1 g/m^2 to about 10 g/m^2.

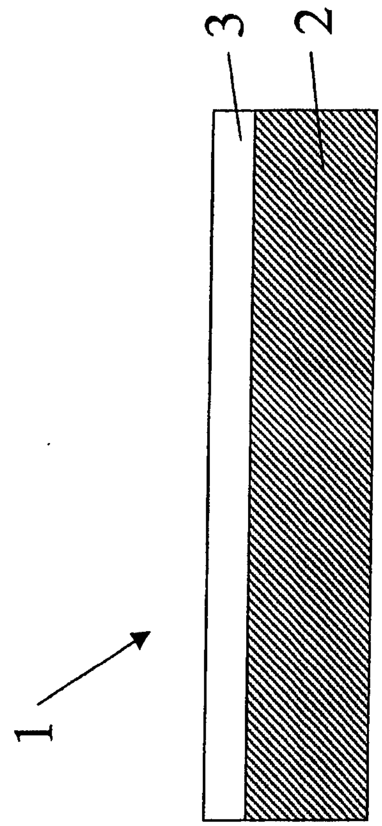

FIG. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2006/033759

A. CLASSIFICATION OF SUBJECT MATTER
INV. B41M5/52 C09D175/08 C09D175/04 C08K3/36
ADD. B41M5/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B41M C09D C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 02/062894 A (AVERY DENNISON CORP.) 15 August 2002 (2002-08-15) claims 1,2,6,17,18 page 7, line 25 page 24, line 3 - line 5 page 25, line 6 page 32, line 23 - line 24 examples 2,9	1-16
X	WO 2004/082952 A (AVERY DENNISON CORP.) 30 September 2004 (2004-09-30) claims 1-4,14-17,20 paragraph [0029] paragraph [0034] example 2	1-6, 12-16

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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Date of the actual completion of the international search	Date of mailing of the international search report
17 January 2007	30/01/2007

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Dardel, Blaise

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2006/033759

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 755 425 A (MINNESOTA MINING AND MFG. CO.) 5 July 1988 (1988-07-05) claim 1 column 2, line 61 - line 64 column 3, line 20 - line 21 column 4, line 48 - column 5, line 20 table 3 -----	1-16
X	US 2003/158322 A1 (BAYER POLYMERS LLC) 21 August 2003 (2003-08-21) claim 1 paragraph [0024] paragraph [0044] - paragraph [0045] paragraph [0053] paragraph [0058] paragraph [0089] - paragraph [0094] table 5 -----	1-16

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2006/033759

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
WO 02062894	A	15-08-2002	BR	0116886	A	09-02-2005
			CA	2437439	A1	15-08-2002
			EP	1368427	A1	10-12-2003
			MX	PA03006967	A	29-01-2004
			PL	363350	A1	15-11-2004
WO 2004082952	A	30-09-2004	AU	2004221871	A1	30-09-2004
			BR	PI0408129	A	01-03-2006
			CA	2519486	A1	30-09-2004
			EP	1601525	A2	07-12-2005
			KR	20050109557	A	21-11-2005
US 4755425	A	05-07-1988	ZA	8801391	A	25-10-1989
US 2003158322	A1	21-08-2003	AU	7051201	A	03-12-2001
			BR	0110999	A	08-04-2003
			CA	2410035	A1	20-11-2002
			CN	1430641	A	16-07-2003
			CZ	20023780	A3	12-02-2003
			DE	10025304	A1	29-11-2001
			WO	0190229	A1	29-11-2001
			EP	1290074	A1	12-03-2003
			HK	1057225	A1	24-02-2006
			HU	0302018	A2	29-09-2003
			JP	2003534423	T	18-11-2003
			MX	PA02011467	A	06-06-2003
			PL	358749	A1	23-08-2004